

niobium atom in $y = 1/4$ and the remainder of these atoms in $y = 3/4$ have not been successful.

Further refinement of these structures is now in progress.

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(—)-Torreyol ("δ-Cadinol")*

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Torreyol, a dextrorotatory sesquiterpene alcohol,¹⁻³ was first isolated in 1922 from the leaves of *Torreya nucifera* Sieb et Zucc. (Taxaceae).¹ Several compounds, e.g. "(+)-δ-cadinol"⁴ and "sesquigoyol",^{5,6} occurring in some pines,⁴⁻⁶ have been shown to be identical with (+)-torreyol.

"Albicaulol" from *Pinus albicaulis* Engelm.⁷ is identical^{3,6} with (—)-torreyol. It has been isolated from other pine species,⁸⁻¹⁰ as well as from many other conifers^{11,17} and it has been described under various synonyms, such as "pilgerol"¹² and "δ-cadinol".¹³ It also occurs in an angiosperm, *Cedrela odorata*, Meliaceae

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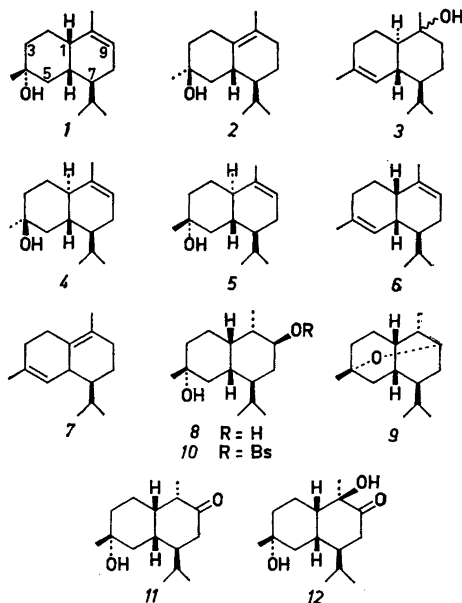
("cedrelanol")¹⁴ and in a cryptogam, the alga *Dictyopteris divaricata* (Phaeophyta) ("brown alga cadinol").¹⁵ Lambertol from *Pinus lambertiana* Dougl. is probably either (+)- or (—)-torreyol.⁸

In view of its priority, we suggest the name torreyol be retained and used instead of the many synonyms.

Different structures, (2),¹³ (3),¹⁶ (4),¹⁷ and (5),¹⁴ have been proposed for torreyol, but none of them appeared to us to be definitely ascertained. (—)-Torreyol has now been found to be represented by formula (1).

On treatment with hydrogen chloride torreyol gave a mixture, as shown by its IR spectrum,¹⁸ of cadinene dihydrochloride and muurolene dihydrochloride, indicating *cis* ring junction in the alcohol. Under the same conditions, cadinenes and cadinols (*trans* ring junction) do not give any muurolene dihydrochloride. Torreyol was proved to be a muurolol in the following way.

(—)-Torreyol was refluxed with an equivalent amount of brosyl chloride in pyridine for 4 h. Without removal of the solvent, the reaction mixture was filtered through basic alumina. Elution with light petroleum gave a mixture of olefins, which, according to GLC (conditions and retention data, see Ref. 9), consisted of three components: an unidentified hydrocarbon (almost same



retention time as γ -muurolene¹⁸), α -muurolene (6)¹⁸ and δ -cadinene (7) in the ratio 20:70:10. α -Muurolene (contaminated by ca. 3% of δ -cadinene) was isolated by argentative column chromatography and identified by its IR spectrum and optical rotation $[\alpha]_D^{22} -91^\circ$.¹⁰

Assuming that the formation of α -muurolene from torreyol proceeds without rearrangement, these results show that the alcohol is a muurolol. Confirmation of this assignment, as well as determination of the orientation of the hydroxyl group in torreyol was achieved by conversion of the alcohol into a cyclic ether.

Hydroboration-oxidation of (-)-torreyol in ethereal solution gave the diol (8) m.p. 128°. This diol was treated with an equimolar quantity of brosyl chloride in pyridine at room temperature for 3.5 h. Without removal of the solvent, the reaction mixture was chromatographed on silica gel. The main product, C₁₅H₂₆O, $[\alpha]_D^{20} +43^\circ$ (c 1.2, CHCl₃), M.W. 222 (mass spec.) obtained in 72% yield showed strong IR absorption bands at 979 and 952 cm⁻¹, but no bands indicating the presence of hydroxyl groups or double bonds. These results proved that the product obtained was a cyclic ether.

The ether bridge must connect carbon atoms 4 and 9. From the sequence of reactions just described, such a cyclic ether can only be obtained from an alcohol possessing *cis*-fused rings and a hydroxyl group orientated as shown in formula (I).

The configuration of the diol (8) at C-9 was apparent from the way in which it was formed (approach of diborane from the much less hindered α -side). The *trans* relationship between the hydroxyl groups in the diol (8) explains the great ease of formation of the ether (9) *via* the hydroxy-ester (10) by an intramolecular nucleophilic substitution reaction.

In view of the flexibility of the *cis*-octalol ring system of torreyol, it is not surprising that contradictory conclusions have been drawn^{13,17,14} concerning the axial or equatorial orientation of the hydroxyl group in torreyol.

The Cotton effect curves of two ketones derived from (-)-torreyol were found by Dauben *et al.*¹⁷ to favour structure (4) for the alcohol. However, the ORD data¹⁷ are also consistent with structure (I) for (-)-torreyol. The two ketones studied by Dauben¹⁷ should now be represented by formula (11) and (12), respectively. Being *cis*-decalones, they may assume such con-

formations as to show the observed Cotton effects.

The absolute configurations of (+)- and (-)-torreyol follow from their correlation with (+)- and (-)-cadinene dihydrochloride, respectively, of known¹⁹ absolute configuration. Formula (I) represents the absolute configuration of (-)-torreyol.

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